

Short communication

Rapid preparation of starch maleate half-esters[☆]Atanu Biswas^{*}, R.L. Shogren, S. Kim, J.L. Willett*National Center for Agricultural Utilization Research, USDA/Agricultural Research Services, 1815 N. University Street, Peoria, IL 61604, USA*

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Abstract

A novel method for the rapid preparation of starch esters is described herein, by rapid heating using microwave or conventional means. A 5-min method to prepare starch maleates with degree of substitution (DS) up to 0.25 was developed when microwave or conventional source assisted fast heating of starch in dimethyl sulfoxide (DMSO) reacted with 0.5 equiv. maleic anhydride in the presence of 0.5 equiv. of pyridine with a reaction efficiency of 50%. For a given amount maleic anhydride higher amount pyridine gave higher DS. The reactivities of maleic and succinic anhydrides were compared. Succinic anhydride/starch gave DS of 0.3 as compared to only 0.1 with maleic anhydride/starch. The effects of varying reaction time, microwave power, anhydride and pyridine amount on the reaction yield and composition were studied. Proton NMR and IR were used to determine the DS. Instead of microwave when reactions were heated with a conventional heat source, starch esterification reactions gave starch maleate with lower DS.

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Keywords: Starch; Starch maleate half-esters; Microwave; Synthesis**1. Introduction**

Among the industrial materials, starch is one of the cheapest and most cost-effective. It is currently used industrially as coatings and sizing in paper, textiles and carpets, as binders and adhesives, as absorbants, and as encapsulants (Whistler & BeMiller, 1993; Whistler, BeMiller, & Paschall, 1984). Starch is often esterified to improve its end-use properties.

Acetylation or succinylation of starch is well documented (Shogren, 2003). Another derivative, maleic anhydride modified starches have many uses, such as in sealing adhesives and paper laminating adhesives formulations. The salts of maleated starch are useful as bread softening agents and an inhibitor for the gelation of starches (Thomas, 1976). For over 50 years, starch maleates and other starch half-esters with industrially useful properties have been prepared via reaction of starch with cyclic anhydrides (Trubiano, 1986).

Starch maleates have been prepared by the reaction in an alkaline aqueous suspension of starch with maleic anhydride (Caldwell, 1945). Reactions in organic media have been performed by Paschall and Katzbeck, (1959). Solvent-free reactions have also been performed by Kovats (1973). These reactions typically require hours for completion and yield low DS products.

Recently, there has been increased interest in microwave heating as a method to facilitate difficult reactions. Yu (1996) hydrolyzed starch to glucose under microwave irradiation.

In this work, we sought to improve its method for the preparation by increasing reaction efficiency and decreasing the reaction time. The rapid reaction of starch with MA in DMSO was achieved under microwave irradiation. The effects of varying reaction time, microwave power, MA and pyridine amount on the reaction yield and composition were studied. Five minutes of microwave heating were sufficient to realize products with DS up to 0.05, and, using pyridine as a catalyst and base, products with DS up to 0.30 were obtained. Proton NMR and IR were used to determine the degree of substitution. For a given amount maleic anhydride higher amount pyridine gave higher DS. Further, the reactivities of MA, succinic anhydride (SA), and octenyl succinic anhydride (OSA) toward starch under microwave irradiation were studied. Finally, we studied the starch/MA/pyridine reaction using both microwave and conventional heat source.

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2. Experimental

2.1. Chemicals

Staley food grade Pearl starch that contained 11% moisture was obtained from Tate and Lyle. Maleic anhydride (95%) with up to 5% maleic acid and 99% sodium dihydrogen phosphate, OSA and SA were obtained from Aldrich. Deionized water was used. DMSO, isopropyl alcohol and ethyl acetate were obtained from Fisher Scientific. Deuterium oxide was obtained in ampoules from Cambridge Isotope Laboratories. All chemicals were used without further purification.

2.2. Instrumentation

Microwave reactions were carried out using an Ethos MicroSYNTH 1600 microwave labstation from Milestone. Reactions were performed in a 50 ml quartz pressure vessel, QRS1550 from Milestone. Pierce Reacti-Vial™ glass vials, 10 ml, equipped with magnetic stirrer were used as reactors and Pierce Reacti-Therm™ heating block was used as the conventional heat source. Samples for IR spectra were prepared from 1 mg of powder and acquired on a Nicolet Avator 370 midrange Fourier transform infrared spectrometer using a SenIR Duroscope diamond ATR. NMR samples were prepared from 10 mg of starch ester and 10 mg of 40% sodium deuteroxide in 0.7 ml of deuterium oxide (NaOD and D₂O that were obtained from Cambridge Isotope Laboratories) heated at 80 °C with stirring for an hour. NMR spectra were obtained by using Bruker Instruments DRX 400 spectrometer.

2.3. Synthesis of starch maleate in DMSO

A mixture of starch (3 g, approximately 17.0 mmol of anhydroglucose units or AGU), 0.91 g. (8.5 mmol or 0.55 equiv.) of maleic anhydride, 0.75 ml (8.5 mmol or 0.55 equiv.) of pyridine and 6 ml of DMSO were added to the reaction vessel and stirred to form a smooth suspension. The microwave program was run immediately with simultaneous magnetic stirring of the reaction mixture. It took 2.5 min to reach 100 °C and we hold at that temperature for another 2.5 min. When the mixture had cooled to 80 °C reaction mixture was blended in ca. 40 ml of isopropyl alcohol for about 3 min, and the resulting fine white powder was collected by vacuum filtration. The powder was subsequently stirred in ca. 40 ml of acetone for 15 min and collected by vacuum filtration. After the product was dried overnight in a vacuum oven at (75 °C), it was subjected to a soxhlet extraction (ca. 5 h) using ethyl acetate to remove the free maleic anhydride and finally the modified starch was dried again. Soxhlet wash was efficient to remove the unreacted MA. However, washing with isopropanol in a blender gave similar results. In the proton NMR very small peaks at 7–8.5 ppm typical of pyridine suggested the presence of trace amount of pyridine in these starch maleate half esters. Yield of these reactions were more than 90%.

In a 10 ml Pierce Reacti-Vial™ glass vial equipped with magnetic stirrer a mixture of starch and anhydrides were heated using a Pierce Reacti-Therm™ heating block as the conventional heat source. This heating rate was same as what we used for microwave heating, i.e. 3.0 min to reach 100 °C and 2.5 min hold at that temperature.

2.4. Degree of substitution

The DS of the starch maleate ester was determined by ¹H NMR using the ratio of the 1/2 alkene two olefin proton absorbance at 6.2 ppm divided by 1/7 of the total starch CH areas, i.e. at 3.3–3.9 (6H) and 5.2 (1H) ppm. Similarly, succinate DS was estimated by 1/4 of the succinate four protons at 2.4 ppm divided by 1/7 of the total starch CH protons. Octenyl succinate DS was calculated by 1/2 of the area of two olefin proton peaks at about 5.3–5.5 ppm divided by 1/7 of the total starch CH areas, i.e. at 3.3–3.9 (6H) and 5.2 (1H) ppm.

2.5. Intrinsic viscosity

Intrinsic viscosities of starch esters hydrolyzed in 1 M KOH were determined following the method of Mark and Mehltretter (1970).

3. Results and discussion

Microwave heating of a polar solvent differs little in comparison to conventional heating. Generally, speaking, the reaction is accelerated under microwave conditions mainly due to the speed with which a mixture can be heated and the high temperatures easily obtainable in pressurized vessels. DMSO is a good solvent for reactions in microwave since it absorbs microwave radiation very well and heats up rapidly.

An attempt was made to find a microwave assisted speedy method of the preparation of starch maleates with varying levels of modification up to 0.25 DS by varying the process parameters, Fig. 1. The parameters were reaction time, temperature, amount of MA and pyridine. We observed that reaction time and temperature had no significant effect on the DS, whereas the pyridine and MA amounts were important.

When starch was reacted with 0.5 equiv. of MA without any base or acid scavenger, depending upon reaction time and temperature we obtained DS in the range of 0.05–0.1. At 100 °C the highest DS of 0.1 was obtained, Fig. 2. The DS does not increase above 0.1 even with excess MA amount. At higher MA level, due to higher acidity probably the formation and hydrolysis of ester both become rapid and as a result the net

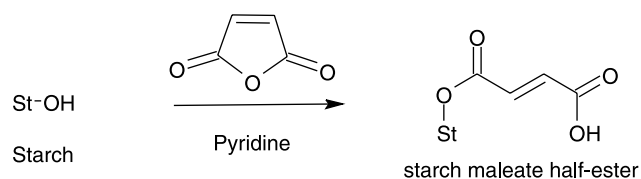


Fig. 1. Reaction of starch with maleic anhydride.

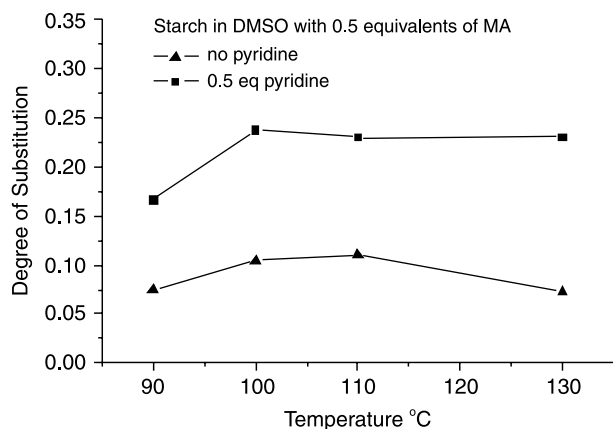


Fig. 2. Effect of reaction temperature on DS.

ester formation remains at 0.1. The same reactions when carried in the presence of 0.5 equiv. of pyridine at 90 and 100 °C gave DS of 0.17 and 0.25, respectively. However, above 100 °C there was no further increase in DS. Thus, we concluded that 100 °C was the optimum reaction temperature.

The same reaction when carried in the presence various amount of pyridine and 0.5 equiv. of MA, gave DS in the range of 0.05–0.25, Fig. 3. The highest DS of 0.25 was obtained for 0.5 equiv. of MA and pyridine. However, DS decreases when pyridine amount exceeded 0.5 equiv. However, when both MA and pyridine were increased to 0.75, 1.0 and 1.5 the DS decreased, Fig. 4. It appears that extra pyridine has no effect on DS and may be hydrolyzing the ester slightly. On the other hand with 0.5 equiv. of pyridine the DS increased with increasing amount of MA. A maximum DS of 0.34 was obtained with 2 equiv. of MA, Fig. 5. However, both 0.5 and 1.0 equiv. of MA gave the same DS of about 0.24. Similarly, 2.0 equiv. gave DS of 0.30 as compared to 0.34 that was obtained with 1.5 equiv. of MA. The higher DS with the increase of MA for a given amount of 0.5 equiv. of pyridine is also shown in the FTIR spectra, Fig. 6. When the 1700–1750 cm^{-1} range is expanded, the ester carbonyl shows up at 1726 cm^{-1} and the carboxylic acid appears 1705 cm^{-1} .

A study to compare the reactivity of three commonly used anhydrides such as MA, SA and OSA with starch was

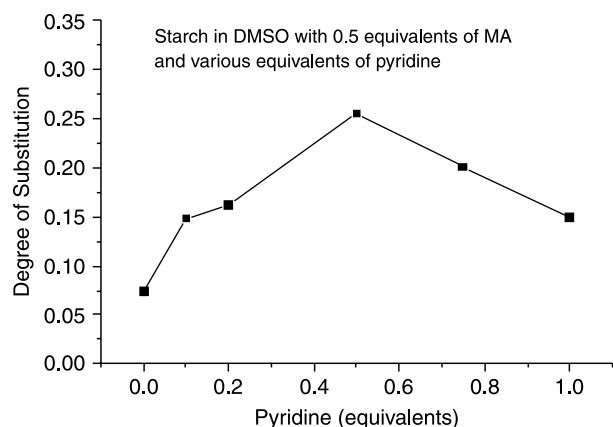


Fig. 3. Effect of pyridine on DS.

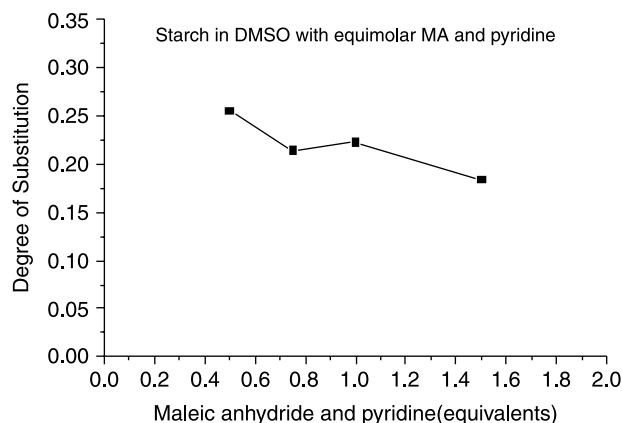


Fig. 4. Effect of pyridine/MA (1:1) amount on DS.

conducted. In DMSO without pyridine, succinic anhydride/starch gave DS of 0.3 as compared to only 0.1 with maleic anhydride/starch. We believe that higher acidity of the acid group of half-ester of maleic acid ($\text{pK}_{\text{a}1}$ of 1.81) than succinic ($\text{pK}_{\text{a}1}$ of 4.2) caused more hydrolysis of the product maleate ester and thus, resulted lower DS. Similarly, OSA also reacted to give starch ester with DS of 0.3.

We found that for a given rate and time of heating microwave gave higher DS and slightly higher yield as compared to conventional heating. Instead of microwave when reactions were heated with a conventional heat source such as Pierce Reacti-Therm™ heating block, we obtained starch maleate with lower DS. Starch, maleic anhydride (0.5 equiv.) and pyridine (0.5 equiv.) were reacted for 5.5 min to give the half ester with DS 0.13, in 80% yield as compared to DS of 0.25 and 90% yield obtained from microwave heating. Thus, conventional heating gave esters with about half the DS value of that obtained from microwave-assisted reaction.

Intrinsic viscosities for starches reacted with 1.0, 0.75 and 0.5 equiv. of maleic anhydride and pyridine were 90, 44 and 30 ml/g, respectively. These values are all lower than the intrinsic viscosity for native corn starch in 1 M KOH

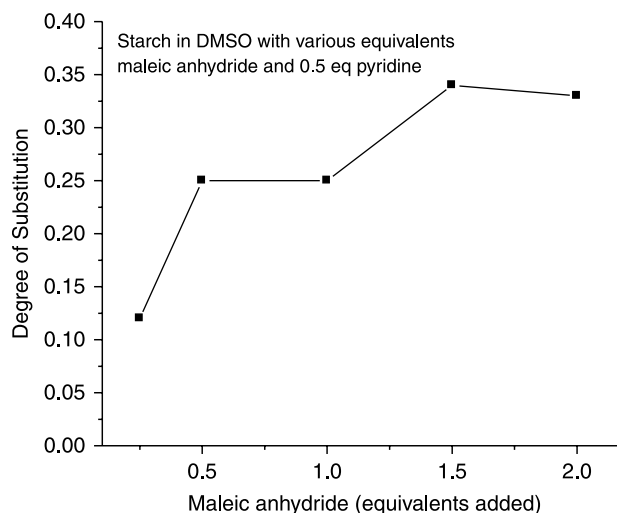


Fig. 5. Effect of MA (with 0.5 equiv. pyridine) on DS.

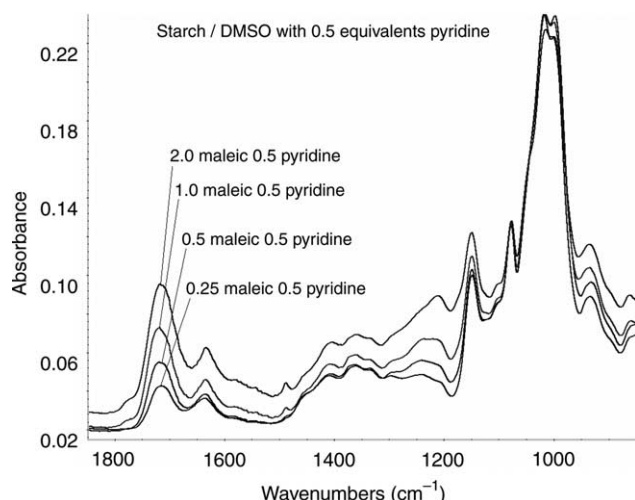


Fig. 6. IR spectra: effect of MA amount on DS.

(170 ml/g) and indicate that some hydrolysis of the glycosidic linkage occurred during reaction. As mentioned above, this is likely due to the acidity of maleic acid, which is formed after hydrolysis of maleic anhydride. The decrease in starch hydrolysis with increasing maleic anhydride/pyridine was probably due to consumption of water in the reaction mixture (from the starch) by reaction with maleic anhydride.

4. Conclusions

A microwave assisted 5 min method to prepare starch maleates with DS up to 0.25 was developed. The DS of 0.25 was obtained when starch in DMSO reacted with 0.5 equiv. maleic anhydride in the presence of 0.5 equiv. of pyridine with a reaction efficiency of 50%. The reaction time and temperature and various microwave programs did not affect the DS significantly. Viscosity studies indicated that some hydrolysis of the glycosidic linkage occurred during reaction. In the

absence of pyridine OSA and SA gave starch esters with DS of 0.3 as compared to 0.1 with MA. This was due to higher acidity of the acid group of half-ester of maleic acid (pK_{a1} of 1.81) than succinic (pK_{a1} of 4.2), which caused more hydrolysis of the product maleate ester. Microwave irradiation did provide advantage over conventional heating for starch esterification reactions. It gave starch maleate with higher in higher yield.

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